



Comparisons of TGA and DSC approaches to evaluate nitrocellulose thermal degradation energy and stabilizer efficiencies

Chun-Ping Lin^{a,*}, Yi-Ming Chang^b, Jai P. Gupta^{c,d}, Chi-Min Shu^b

^a Department of Health and Nutrition Biotechnology, College of Health Science, Asia University, 500, Lioufeng Rd., Wufeng, Taichung 41354, Taiwan, ROC

^b Process Safety and Disaster Prevention Laboratory, Department of Safety, Health, and Environmental Engineering, National Yunlin University of Science and Technology, 123, University Rd., Sec. 3, Douliou, Yunlin 64002, Taiwan, ROC

^c Rajiv Gandhi Institute of Petroleum Technology, Rae Bareilly 229316, UP, India

^d Department of Chemical Engineering, Indian Institute of Technology, Kanpur 208016, UP, India

ABSTRACT

This study investigated the thermal degradation energy (activation energy, E_a) for nitrocellulose (NC) with low nitrogen content of 11.71 mass%, so-called NC3, by using two different kinds of thermal analysis instruments: thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC). A comparison of E_a for various nitrogen content NC samples at two scanning rates (5 and 10 °C min⁻¹) tested by TGA and DSC is also discussed in this paper. Meanwhile, our aim was to analyze the anti-degradation of E_a for NC with high nitrogen content, as so-called NC1. Thermal stability for NC1 with diphenylamine (DPA) was tested via DSC with 10 DPA concentrations in weights of 0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75, 2.0, and 3.0 mass%. Experimental results indicated that E_a of NC3s was 319.91 kJ mol⁻¹. Moreover, that while dosing DPA into NC1 the best recipe could be employed to avoid any violent NC1 runaway and also can be used to distinguish the differences of thermal decomposition E_a between NC with different nitrogen contents. This study established a fast and efficient procedure for thermal decomposition properties of NC, and could be applied as an intrinsically safer design during relevant operations.

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Keywords: Thermal degradation energy (activation energy; E_a); Nitrocellulose (NC); Thermogravimetric analyzer (TGA); Differential scanning calorimetry (DSC); Intrinsically safer design

1. Introduction

We determined the thermal degradation energy (activation energy, E_a) for nitrocellulose (NC) with low nitrogen content by using two different kinds of thermal analysis instruments: thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC). A comparison of activation energy for various nitrogen content of NC samples for two scanning rates (5 and 10 °C min⁻¹) tested by TGA and DSC is also discussed in this paper.

In addition to realizing the E_a of NC analysis through TGA (Regnier, 1997) and DSC (Lin and Shu, 2009) approaches to receive a fast and efficient procedure on thermal decomposition properties for NC, we also compared as to whose approach presented a better mathematical model for the E_a of NC. Thereafter, that thermal analysis approach was used to understand the differences of NC activation energies with different nitrogen content. Also, the influence of different scanning rates and different nitrogen contents on the E_a for NC was discovered.

* Corresponding author at: Department of Health and Nutrition Biotechnology, College of Health Science, Asia University, 500, Lioufeng Rd., Wufeng, Taichung 41354, Taiwan, ROC. Tel.: +886 4 2332 3456x20009; fax: +886 4 2332 1126.

E-mail address: chunping927@gmail.com (C.-P. Lin).

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Nomenclature

A	pre-frequency factor (s^{-1})
C_A	sample concentration (mol L^{-1})
C_p	heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$)
E_a	activation energy (kJ mol^{-1})
k	the rate constant (g s^{-1})
M	molecular weight (g mol^{-1})
m	sample mass (g)
n	reaction order, dimensionless
Q_0	total heat g decomposition (kJ kg^{-1})
Q_t	decomposition heat released at time t (kJ kg^{-1})
R	ideal gas constant ($8.31415 \text{ J K}^{-1} \text{ mol}^{-1}$)
r	reaction rate (g s^{-1})
S	shape index, dimensionless
T	absolute temperature (K)
T_0	onset temperature (K)
T_f	final temperature (K)
T_m	temperature at the maximum rate (K)
t	time (s)
W	actual weight of the sample (g)
W_0	initial weight of the sample (g)
W_∞	final weigh of the sample (g)
α	degree of conversion, dimensionless
ρ	sample density (g L^{-1})
θ	heating rate ($^{\circ}\text{C min}^{-1}$)

As the (–OH) group inside the cellulose was gradually replaced by (–ONO₂), one, two, and three nitrate esters were generated, and their corresponding nitrogen content was 6.75, 11.1, and 14.14 mass%, respectively. In this study, NC with various nitrogen content (11.50–13.60 mass%) was used in the experiments (Brill, 1997; Moore, 1977; Urbanski, 1964; Zheng, 1990).

The application of stabilizer, 1 mass% diphenylamine (DPA), is the standard additive for a single base propellant (Bohn, 1997; Katoh et al., 2007; Singh and Pandey, 2003; Wilker and Heeb, 2007). However, there is a lack of understanding on whether more or less DPA stabilizer could be helpful to enhance the stability of NC1. The stabilizer's influence on thermal decomposition and thermal stability for NC1 was determined (Bohn, 1997; Katoh et al., 2007; Singh and Pandey, 2003; Wilker and Heeb, 2007), which was employed and discussed with adding different dosages of DPA additives to be surveyed by DSC tests.

Consequently, the validity of the results acquired depends significantly on the reliability of the kinetic model applied, which is essentially verified by a suitable choice of a mathematical model of a reaction and the correctness of the methods used for the kinetic evaluation. These approaches can be used for many crucial tasks, such as conceptual design and optimization of chemical processes, reactor design, assessment of reaction hazards, and choice of safer conditions of storage and transportation of chemicals, etc.

2. Material and methods

2.1. Instruments

Instruments used in this study were:

Electrical oven: risen universal oven.

Differential scanning calorimetry (DSC): Netzsch DSC 200, Germany.

Thermogravimetric analyzer (TGA): Universal V2.4F Instruments, USA.

Element analyzer (EA): PerkinElmer Model 2400 CHN, USA.

2.2. Samples

All the samples were obtained from a domestic arsenal of the Republic of China (ROC) in Taiwan. The nitrogen content of NC1, NC2, NC3 and NC4 was 13.57, 13.47, 11.71 and 11.55 mass%, respectively. Results of elemental analysis (EA) tests for NC1, NC2, NC3 and NC4 are listed in Table 1.

2.3. Process of making NC1, NC2, NC3, NC4 into transparent membrane

De-ionized water was carefully pumped in 0.5 g samples of NC1, NC2, NC3 and NC4 using a vacuum pump. The samples were dried in an electrical oven for 4 h at 80 °C, and then poured into a one-neck round bottom flask (125 mL). After that, 30 mL acetone was added into the flask and stirred sufficiently to completely dissolve the NCs. Then, the acetone was removed by vacuum evaporation. This process yielded a transparent membrane on the inside wall of the flask. Several membranes with 0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75, 2.0, 3.0 mass% of DPA mixed with NC1, NC2, NC3 and NC4 were produced. These transparent membranes were used for TGA and DSC analyses.

2.4. Operating procedure of TGA

Scanning rate: 5 and 10 °C min^{−1}.

Chemical: NC3.

2.5. Operating procedure of DSC

2.5.1. Scanning rates: 5 and 10 °C min^{−1}

Chemicals: NC1, NC2, NC3, NC4.

We used nitrogen as the carrier gas. Its flow rate was 10 mL min^{−1}, and the scanning range of temperature was from 50 to 280 °C.

2.5.2. Scanning rate: 5 °C min^{−1}

Chemicals: different contents of DPA in NC1 (0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75, 2.0, 3.0 mass%).

In all studies with TGA and DSC, nitrogen was the carrier gas. Its flow rate was 10 mL min^{−1}, and the heating range in TGA and DSC was from 50 to 280 °C.

3. Results and discussion

3.1. Determination of E_a by TGA

Like many other organic compounds, NC has a stable molecular structure that only vaporizes, sublimates, or its molecular structure cracks at a high temperature to decompose into gaseous products (Regnier, 1997). This changes the weight of the sample. This weight loss phenomenon has a great relationship with the nature of the nitrocellulose. Since the thermal decomposition has a direct relationship with the stability of the compounds, TGA was used to measure the E_a of NC to determine its stability. The degree of conversion or degradation of the material, α can be calculated by the TGA curve

Table 1 – Results of NC1, NC2, NC3, NC4 EA analyses.

Sample Element	NC1			NC2			NC3			NC4		
	C	H	N	C	H	N	C	H	N	C	H	N
1	25.21	2.62	13.16	25.05	2.63	13.12	27.3	2.72	11.67	27.3	2.8	11.61
2	25.38	2.4	13.56	25.46	2.3	13.3	27.31	2.73	11.74	27.46	2.79	11.48
3	25.57	2.41	13.97	25.55	2.41	13.98	N/A	N/A	N/A	N/A	N/A	N/A
Nitrogen content (wt%)	13.57	13.47	11.71	11.55								

Remarks: The average nitrogen content Nwt% was calculated with the root mean squares.

(Fig. 1):

$$\alpha = \frac{W_0 - W}{W_0 - W_\infty} = \frac{\Delta W}{\Delta W_\infty} \quad (1)$$

where W is the actual weight of the sample; W_0 is the initial weight of the sample and W_∞ is the final weight of the sample. The rate of degradation of the material, $d\alpha dt^{-1}$ is dependent on the temperature and the weight of the sample, and can be expressed as:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (2)$$

$$f(\alpha) = (1 - \alpha)^n \quad (3)$$

where k is the rate constant, n is the reaction order, and $f(\alpha)$ is the conversion functional relationship.

$f(\alpha)$ is the proportional to the concentration of non-degraded or un-reacted material:

The temperature dependence of the rate constant k may be described by the Arrhenius expression:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

Combining Eqs. (2)–(4), the overall rate of loss of reactive material is given by:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) (1 - \alpha)^n \quad (5)$$

The integrated form of Eq. (5) with respect to temperature becomes:

$$\int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = A \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dt \quad (6)$$

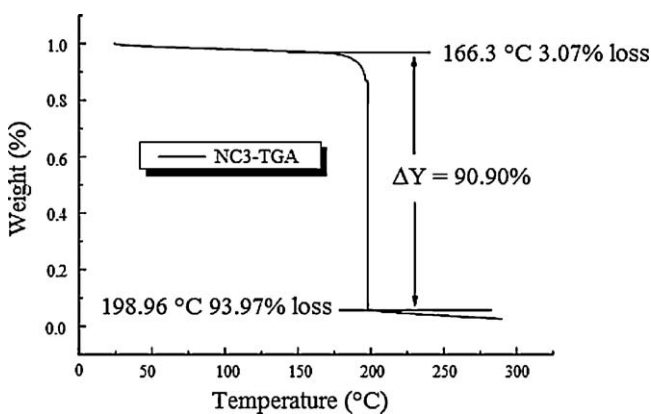


Fig. 1 – TGA curve for NC3.

$$\frac{1 - (1 - \alpha)^{1-n}}{1 - n} = \frac{ART^2}{\theta E_a} \left(1 - \frac{2RT_0}{E_a}\right) \exp\left(-\frac{E_a}{RT}\right) \quad (7)$$

where $\theta = dT dt^{-1}$ (heating rate by TGA test).

Taking the natural logarithm on both sides, Eq. (8) could be expressed as below:

$$\text{For } n \neq 1 \text{ or } n \neq 0: \ln \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} \right] = \ln \frac{AR}{\theta E_a} \left(1 - \frac{2RT_0}{E_a}\right) - \frac{E_a}{RT} \quad (8)$$

The values of $\ln\{[1 - (1 - \alpha)^{1-n}]T^{-2}(1 - n)^{-1}\}$ versus T^{-1} were plotted as straight lines for each NC sample. Fig. 2 is for NC3. The heat of decomposition is obtained from the slope $= -E_a R^{-1}$.

Many decomposition reaction orders are neither for $n \neq 1$ nor for $n \neq 0$. The Kissinger method allows the calculation of activation energy from a point T_m which is temperature at the maximum rate when $d\alpha dt^{-1}$ is zero (Kissinger, 1957; Regnier, 1997). Here, the differentiation of Eq. (5) with respect to time and setting the resulting expression equal to zero gives:

$$\begin{aligned} \frac{d}{dt} \left(\frac{d\alpha}{dt} \right)_{\max} &= 0 = \left(\frac{d\alpha}{dt} \right)_{\max} \\ \frac{d}{dt} \left(\frac{d\alpha}{dt} \right) &= \frac{d\alpha}{dt} \left[\frac{E_a(dT/dt)}{RT^2} - An(1 - \alpha)^{n-1} \exp\left(-\frac{E_a}{RT}\right) \right] = 0 \\ \frac{E_a(dT/dt)}{RT_m^2} &= An(1 - \alpha)^{n-1} \exp\left(-\frac{E_a}{RT_m}\right) \end{aligned} \quad (9)$$

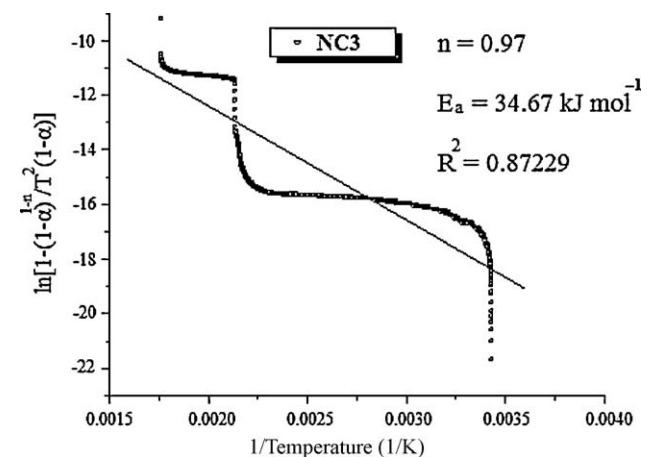


Fig. 2 – TGA graphical analysis for NC3 activation energy (full range).

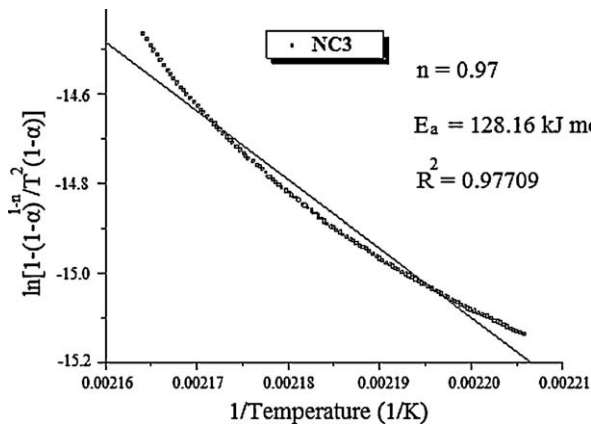


Fig. 3 – TGA thermal analysis of NC3 when the scanning rate is 5 °C min⁻¹ (between initial conversion to the accelerating conversion).

where T_m is the temperature at the maximum degradation rate for the sample.

$$\frac{dT}{dt} = \frac{ART_m^2}{E_a} n(1-\alpha)_m^{n-1} \exp\left(-\frac{E_a}{RT_m}\right) \quad (10)$$

The Kissinger method has shown that the product $n(1-\alpha)_m^{n-1}$ is independent of the scanning rate (Regnier, 1997). Similarly, taking the natural logarithm of Eq. (10), Eq. (11) is obtained:

$$\ln\left(\frac{\theta}{T_m^2}\right) = -\left(\frac{E_a}{RT_m}\right) \quad (11)$$

The plot of $\ln(\theta/T_m^2)$ versus T_m^{-1} renders a straight line and the slope ($-E_a/R$).

The decomposition of NC is a complicated automatic chain reaction (Brill, 1997; Chu, 1994; Lin and Shu, 2009; Zheng, 1990). The NC has the maximum degradation reaction rate uncertainty at the $d(dT/dt)/dt = 0$.

A solid decomposition reaction may take place by any one of a number of elementary mechanisms, as well as a combination of these mechanisms (Brill, 1997; Chu, 1994; Zheng, 1990). Thus, it is difficult to find an exact meaning for the reaction order n of a nitrocellulose thermal decomposition determined by Kissinger index of shape equation (Kissinger, 1957; Regnier, 1997):

$$S = \frac{a}{b} \rightarrow n = 1.26\sqrt{S} \quad (12)$$

where S is the shape index of the differential thermal analysis. The shape index is defined as the absolute value of the ratio of the slope of tangents to the curve at inflection points (Kissinger, 1957; Regnier, 1997). The values of $\ln\{[1-(1-\alpha)^{1-n}]T^{-2}(1-n)^{-1}\}$ versus T^{-1} are indicated in Fig. 2. The straight line was acquired by substituting the reaction order n by Kissinger's index of shape equation and the heat of decomposition from slope $= -E_a/R$. Here, NC3 has been used as an example. E_a can be calculated through the graphical analysis for NC3 (5 °C min⁻¹), as shown in Fig. 2.

From Fig. 2, the linear trend is not as good as expected from TGA analysis as can be observed, which was even far from that (ca. 160–240 kJ mol⁻¹) as reported in the literature (Brill, 1997; Chu, 1994; Lin and Shu, 2009; Urbanski, 1964; Zheng, 1990). The value retrieving range is between initial conversion

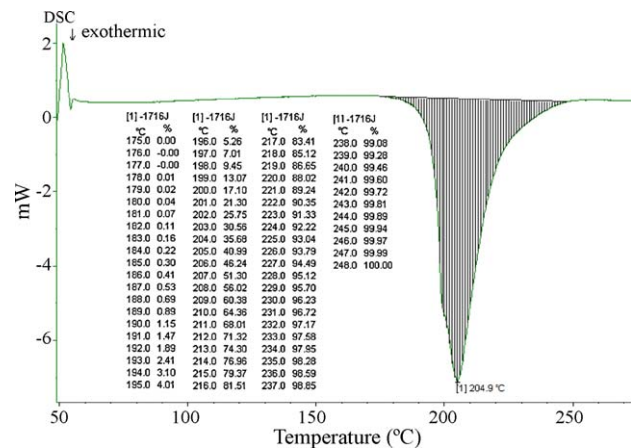


Fig. 4 – DSC thermal curve of NC3 when the scanning rate is 5 °C min⁻¹.

to the accelerating conversion ($180.34^\circ\text{C} \leq T \leq 189.07^\circ\text{C}$), while the TGA analysis range was $0.053 \leq \alpha \leq 0.106$ (Fig. 3).

Fig. 3 shows that values in this range conducted with the TGA approach produced a better linear trend, and the thermal decomposition E_a (128.16 kJ mol⁻¹) is closer to that in the literature (ca. 160–240 kJ mol⁻¹) (Brill, 1997; Chu, 1994; Lin and Shu, 2009; Urbanski, 1964; Zheng, 1990).

3.2. Determination of E_a by DSC

We examined NC3 with DSC, to acquire some thermokinetic parameters, and then modified the Arrhenius equation to fit the activation energy of nitrocellulose on decomposition (Lin and Shu, 2009).

To expedite the model development, we first set T_0 and T_f as onset temperature and final temperature for runaway excursion. Meanwhile, Q_0 and Q_t are the total heats of decomposition and the heat released by the decomposing material at time t .

The degree of conversion can be computed on the basis of the DSC curve. The NC3 DSC curve is depicted in Fig. 4.

$$\alpha = \frac{mC_p(T_f - T)}{mC_p(T_f - T_0)} = \frac{(T_f - T)}{(T_f - T_0)} \quad (13)$$

in which m and C_p are sample mass and sample heat capacity, then

$$1 - \alpha = 1 - \frac{(T_f - T)}{(T_f - T_0)} = \frac{(T - T_0)}{(T_f - T_0)} \quad (14)$$

Based on the Arrhenius equation:

$$-r_A = -\frac{dC_A}{dt} = kC_A^n = A \exp\left(-\frac{E_a}{RT}\right)C_A^n \quad (15)$$

where r_A is the reaction ratio; C_A is the sample concentration; k is the reaction rate constant; n is the reaction order; A is the pre-exponential factor; E_a is the activation energy; T is the absolute temperature; R is the gas constant.

Let

$$C_{A0} = \frac{\rho}{M} \quad (16)$$

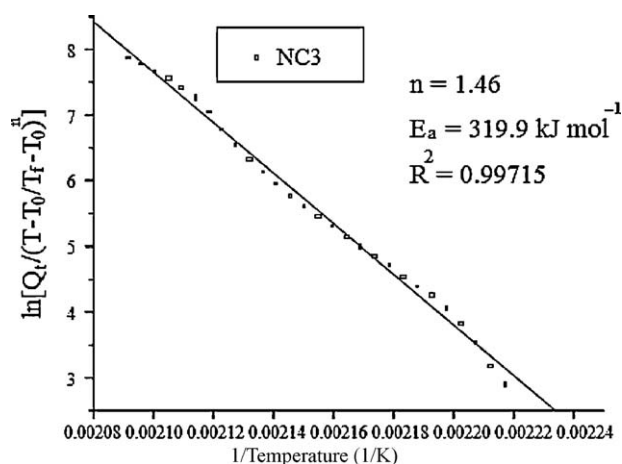


Fig. 5 – Activation energy by analytical graph for NC3 ($5^{\circ}\text{C min}^{-1}$).

where ρ is the sample density; M is the molecular weight, and C_{A_0} is the initial concentration of the sample:

$$C_A = C_{A_0}(1 - \alpha) \quad (17)$$

We obtain the following equation by combining Eq. (14) with Eq. (17) and substituting into Eq. (15).

$$\begin{aligned} -\frac{dC_A}{dt} &= AC_{A_0}^n (1 - \alpha)^n \exp\left(-\frac{E_a}{RT}\right) \\ &= AC_{A_0}^n \left(\frac{T - T_0}{T_f - T_0}\right)^n \exp\left(-\frac{E_a}{RT}\right) \end{aligned} \quad (18)$$

From the non-isothermal curve (Fig. 4) we can observe that the heat of decomposition varies with the reaction rate. Therefore, Eq. (19) can be expressed as follows:

$$Q_t = AQ_0 C_{A_0}^n \left(\frac{T - T_0}{T_f - T_0}\right)^n \exp\left(-\frac{E_a}{RT}\right) \quad (19)$$

Dividing $[(T - T_0)/(T_f - T_0)]^n$ on both sides of Eq. (19), and then taking the natural logarithm on both sides, we have Eq. (20):

$$\ln\left(\frac{Q_t}{[(T - T_0)/(T_f - T_0)]^n}\right) = \ln AQ_0 C_{A_0}^n - \frac{E_a}{RT} \quad (20)$$

The values of $\ln[Q_t(T - T_0)/(T_f - T_0)^n]$ versus T^{-1} are plotted in Fig. 5. A straight line by substituting the appropriate reaction order n was acquired, along with the heat of decomposition from slope $= -E_a R^{-1}$.

Fig. 4 shows the DSC thermal curve with scanning rate of $5^{\circ}\text{C min}^{-1}$. Analyzing with DSC, the degree of conversion at each time varying point was acquired because nitrocellulose releases energy as the temperature rises. Furthermore, the

total heat of decomposition was obtained by the integration of thermal curves in Fig. 4. It indicates that all the energy was released when the initial decomposing DSC curve bounced back to the baseline.

Similar to the typical explosive property, NC3 possesses nitrate ester groups. Therefore, while the thermal decomposition is being processed, products will be accumulated due to the exothermal reaction, which promotes the reaction to accelerate. This phenomenon is an important characteristic of an explosive's heat of decomposition. Thus, the heat of decomposition of nitrocellulose is a form of auto chain reaction (Brill, 1997; Chu, 1994; Lin and Shu, 2009; Urbanski, 1964; Zheng, 1990).

The E_a of nitrocellulose in this study was limited to its thermal decomposition in the range from the beginning of thermal decomposition to its peak temperature. Containing an intricate automatic chain reaction, the decomposition after the peak temperature, which is not a simple thermal decomposition reaction, is not discussed here. NC3 was again used as an example. E_a can be calculated through an analytical graph for NC3 ($5^{\circ}\text{C min}^{-1}$), as shown in Fig. 5. Comparing the E_a of thermal decomposition ($319.91 \text{ kJ mol}^{-1}$; nitrogen content 11.71 wt%) with that in the literature (Brill, 1997; Chu, 1994; Lin and Shu, 2009; Urbanski, 1964; Zheng, 1990) (ca. $160\text{--}240 \text{ kJ mol}^{-1}$; nitrogen content 12.3–13.35 mass%), we found that DSC could be properly used to study the thermal decomposition E_a of NC.

Comparing the thermal decomposition E_a in terms of different scanning rates, gives a worse correlation coefficient in both TGA and DSC analyses when the scanning rate was at $10^{\circ}\text{C min}^{-1}$. The value excerpction range in TGA approach was very complicated and the model did not apply to it, and hence this led to a poor linear trend. As for the reaction order based on the DTA curve characteristic proposed by Kissinger (Kissinger, 1957; Regnier, 1997), an inferior accuracy on the thermal decomposition E_a was obtained because it contained some errors and the data retrieving process was not accurate. A comparison of TGA and DSC in analyzing the thermal decomposition of NC3 at different scanning rates of 5 and $10^{\circ}\text{C min}^{-1}$ is listed in Table 2.

In contrast, when the model was modulated to follow using DSC analysis on the E_a of NC3, it produced easier, faster, and more accurate linear trend. The E_a analysis had less error than TGA did.

3.3. The sample different scanning rates to analyze NC1, NC2, NC4 by DSC

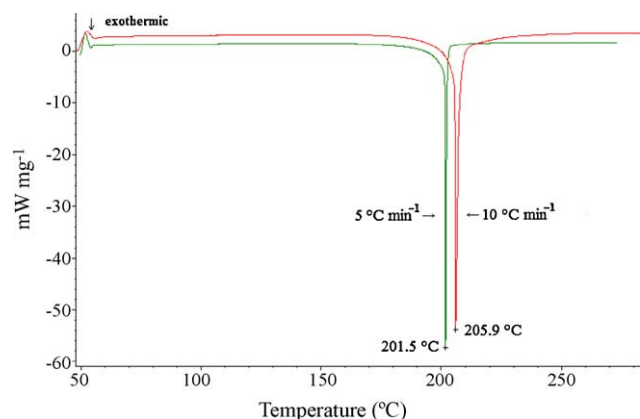
DSC was used with two scanning rates (5 and $10^{\circ}\text{C min}^{-1}$) to analyze NC1, NC2 and NC4 and compare their characteristics for thermal decomposition. Peak temperature is also influenced by the scanning rate. From DSC thermal curves of NC1 and NC2 (Figs. 6 and 7), a delay with the peak temperature was

Table 2 – A comparison of TGA and DSC in analyzing the thermal decomposition of NC3 at different scanning rates of 5 and $10^{\circ}\text{C min}^{-1}$.

Approach of thermal analysis	TGA		DSC	
Scanning rate ($^{\circ}\text{C min}^{-1}$)	5	10	5	10
Reaction order (n)	0.97	1.07	1.46	1.15
E_a (kJ mol^{-1})	128.16	134.78	319.91	388.46
Correlation coefficient, R^2	0.97709	0.96685	0.99431	0.99307
Standard deviation, SD	0.15129	0.03146	0.11328	0.10815
Error (kJ mol^{-1})	2.83	2.65	4.75	7.65

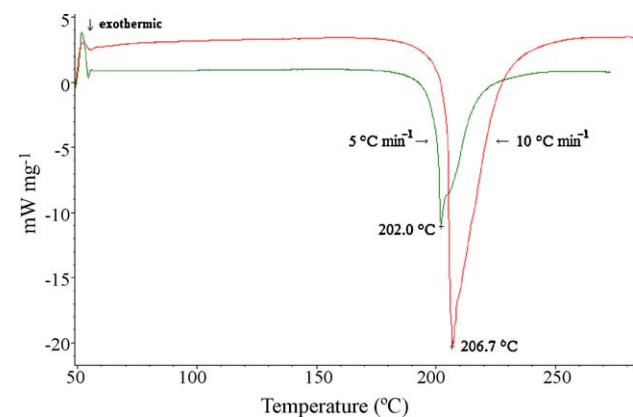
Table 3 – E_a results of NC1, NC2 and NC4 at the scanning rates of 5 and 10 °C min⁻¹ by DSC.

Sample (scanning rate, °C min ⁻¹)	5 °C min ⁻¹			10 °C min ⁻¹		
	NC1	NC2	NC4	NC1	NC2	NC4
Reaction order (n)	1.62	1.53	1.22	1.87	1.34	0.89
E_a (kJ mol ⁻¹)	149.97	239.41	347.27	129.13	268.66	416.51
Correlation coefficient, R^2	0.97308	0.99068	0.99648	0.96666	0.97869	0.99730
Standard deviation, SD	0.13560	0.08619	0.07938	0.10353	0.14401	0.09168
Error (kJ mol ⁻¹)	4.55	2.70	4.50	4.90	8.87	4.43
Nitrogen content (wt%)	13.57	13.47	11.55	13.57	13.47	11.55

**Fig. 6 – DSC thermal curves of NC1 at 5 and 10 °C min⁻¹ scanning rates.**

discerned.

The greater scanning rate may lead to a wide and smooth DSC thermal curve, intending to neglect the slight thermal decomposition differences. As far as NC's characteristics of

**Fig. 7 – DSC thermal curves of NC2 at 5 and 10 °C min⁻¹ scanning rates.**

explosives are concerned, too great a scanning rate may lead to an automatic chain reaction to accelerate the decomposition reaction (Brill, 1997; Chu, 1994; Lin and Shu, 2009; Urbanski, 1964; Zheng, 1990). Therefore, when analyzing the E_a of NC's thermal decomposition, a better condition at the scanning rate of 5 °C min⁻¹ was acquired.

Using DSC tests, the analyzed E_a results of NC1, NC2 and NC4 at different scanning rates are listed in Table 3. In Tables 2 and 3, the more nitrogen an NC contains, the smaller the E_a of thermal decomposition it has. This is because the cellulose of low nitrogen content contains more hydroxyl groups (–OH) while that of high nitrogen content possesses more nitrate ester (–ONO₂) (Brill, 1997; Chu, 1994; Lin and Shu, 2009; Urbanski, 1964; Zheng, 1990). In terms of thermal decomposition, –NO₂ is prone to decompose easier than O–H.

3.4. Different dosages of DPA mixed into NC1 to influence activation energy

From Table 4, we observed that greater dosages of DPA led to lower activation energy. NC1 without DPA has the lowest activation energy (114.36 kJ mol⁻¹), which means that DPA did affect thermal decomposition of NC1. Furthermore, it could be observed that there was a significant increase of E_a in DPA dosages ranging from 0.5 to 1.5 mass%, which indicates there was a better anti-thermal decomposition quality of DPA dosage in this range. The greatest E_a of thermal decomposition (226.91 kJ mol⁻¹) was acquired as the DPA dosage was 0.75 mass%.

In addition, the highest E_a value was obtained at 0.75 mass% of DPA, which was the optimal dosage. The theoretical support had in the process of making a single or double base propellant with 1 mass% of DPA as a standard dosage (Bohn, 1997; Katoh et al., 2007; Singh and Pandey, 2003; Wilker and Heeb, 2007). Therefore, DSC can establish the optimal stabilizer adding system to be widely applied to making different nitrocellulose products.

Table 4 – Influence of different dosages of DPA on NC1's thermal decomposition.

Added proportion (mass%)	Reaction order (n)	E_a (kJ mol ⁻¹)	Correlation coefficient, R^2	Standard deviation, SD	Error (kJ mol ⁻¹)
0.00	1.74	114.36	0.98831	0.08324	2.04
0.25	1.94	135.82	0.97624	0.10822	4.00
0.50	1.51	217.95	0.99566	0.06591	2.88
0.75	1.23	226.91	0.99503	0.08408	2.98
1.00	1.80	184.93	0.99397	0.05836	3.07
1.25	1.33	205.21	0.99337	0.08825	3.11
1.50	1.45	218.10	0.99634	0.06085	2.64
1.75	1.45	168.48	0.97632	0.14862	4.71
2.00	1.30	192.26	0.98919	0.10004	3.87
3.00	1.73	139.39	0.99022	0.09393	2.28

Fortunately, to date, many excellent researches focused on hazardous materials have been conducted and proposed by scientists all around the world (Amyotte et al., 2009; Lin et al., 2009; Pekalski and Pasman, 2009). Therefore, it is anticipated that this study can help the relevant plants or processes to avoid thermal accidents.

4. Conclusions

This study has established a fast and accurate analysis model on E_a of nitrocellulose for thermal decomposition. In addition to realizing nitrocellulose's thermal decomposition E_a analysis through TGA and DSC approaches, it was concluded that the DSC approach presented a better mathematical model for NC's E_a of thermal decomposition. Moreover, the influence of different scanning rates on thermal decomposition E_a was discovered.

The conclusions reached are as follows:

- (1) The DSC approach had a better reliability on analyzing E_a NC for thermal decomposition. Furthermore, a fixed and easier mathematical model for value retrieving range was received.
- (2) In light of NC's thermal decomposition characteristic, DSC can be used to distinguish the differences of thermal decomposition E_a between NC with different nitrogen contents.
- (3) To conduct NC's E_a of thermal decomposition, better results at a slower scanning rate of 5°C min^{-1} were obtained.
- (4) DSC analyses can be facilitated to acquire NC1's best stabilizer's additive dosage (0.75 mass%).

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